

# **EMISSIONS AND LUBRICITY EVALUATION OF RAPESEED DERIVED BIODIESEL FUELS**

**By**

**Christopher A. Sharp**

**FINAL REPORT**

**Prepared for**

**MONTANA DEPARTMENT OF  
ENVIRONMENTAL QUALITY  
P.O. Box 202301  
Helena, Montana 59620**

**November 1996**

**SOUTHWEST RESEARCH INSTITUTE  
P.O. Drawer 28510  
San Antonio, Texas 78228-0510**

# **EMISSIONS AND LUBRICITY EVALUATION OF RAPESEED DERIVED BIODIESEL FUELS**

**By**

**Christopher A. Sharp**

**FINAL REPORT**

**Prepared for**

**MONTANA DEPARTMENT OF  
ENVIRONMENTAL QUALITY  
P.O. Box 202301  
Helena, Montana 59620**

**November 1996**

**Reviewed by:**

**Approved by:**

---

**Terry L. Ullman, Manager  
Department of Emissions Research  
Automotive Products and  
Emissions Research Division**

**Charles T. Hare, Director  
Department of Emissions Research  
Automotive Products and  
Emissions Research Division**

## TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES .....	iii
LIST OF TABLES .....	v
EXECUTIVE SUMMARY .....	vi
I. INTRODUCTION .....	1
II. DESCRIPTION OF PROGRAM .....	2
A. Test Engine .....	2
B. Test Fuels .....	2
C. Test Procedures .....	5
III. TEST RESULTS .....	12
A. Regulated Transient Emissions .....	12
B. Hydrocarbon Speciation .....	28
C. PAH Analysis .....	44
D. Lubricity Testing .....	52
IV. CONCLUSIONS .....	54
APPENDICES	
A. INDIVIDUAL TRANSIENT TEST RESULTS	
B. DETAILED C <sub>1</sub> - C <sub>12</sub> SPECIATION RESULTS	
C. C <sub>1</sub> - C <sub>12</sub> SPECIATION GRAPHS	
D. PAH SUMMARY ASSESSMENT	

## LIST OF FIGURES

<b><u>Figure</u></b>	<b><u>Page</u></b>
1    Transient Test Cell Installation of the Cummins B5.9L Engine for Biodiesel Testing .....	3
2    Graphic Representation of the Heavy-Duty Transient Cycle.....	5
3    Schematic of Mass Spectral Analyses Sampling System .....	8
4    Composite Transient Regulated Emission Levels Without Catalyst.....	17
5    Composition of Transient Particulate Emissions Without Catalyst .....	18
6    Percent Change in Composite Emission Levels Without Catalyst, Biodiesel Fuels Versus Diesel .....	19
7    Composite Transient Regulated Emission Levels With Catalyst.....	20
8    Composition of Transient Particulate With Catalyst .....	21
9    Percent Change in Regulated Emission Levels With Catalyst, Biodiesel Fuels Versus Diesel .....	22
10   Average Transient Torque-Map Data for Cummins B5.9L Engine With Biodiesel Fuels .....	23
11   Catalyst Conversion Efficiency for Regulated Pollutants With Biodiesel Fuels .....	26
12   C1 - C12 Hydrocarbon Mass and Reactivity Without Catalyst .....	29
13   C1 - C12 Hydrocarbon Mass and Reactivity With Catalyst .....	30
14   Mass Spectrograph Data for Different Classes of Compounds in Exhaust, Diesel Fuel.....	37
15   Mass Spectrograph Data for Different Classes of Compounds in Exhaust, REE Fuel .....	38
16   Mass Spectrograph Data for Different Classes of Compounds in Exhaust, RME Fuel.....	39

## LIST OF FIGURES

<b><u>Figure</u></b>	<b><u>Page</u></b>
17 Mass Spectrograph Data for Different Classes of Compounds in Exhaust, REE50 Fuel .....	40
18 Mass Spectrograph Data for Different Classes of Compounds in Exhaust, RME50 Fuel.....	41
19 Mass Spectrograph Data for Different Classes of Compounds in Exhaust, REE20 Fuel .....	42
20 Mass Spectrograph Data for Different Classes of Compounds in Exhaust, RME20 Fuel.....	43
21 PAH Data With and Without Catalyst, Exhaust from 2D and REE Fuels .....	46
22 PAH Data With and Without Catalyst, Exhaust from 2D and RME Fuels.....	47
23 PAH Data With and Without Catalyst, Exhaust from 2D and REE50 Fuels .....	48
24 PAH Data With and Without Catalyst, Exhaust from 2D and RME50 Fuels.....	49
25 PAH Data With and Without Catalyst, Exhaust from 2D and REE20 Fuels .....	50
26 PAH Data With and Without Catalyst, Exhaust from 2D and RME20 Fuels.....	51
27 Composite HC and CO Levels Versus Oxygen Weight Percent in Fuel Without Catalyst.....	55
28 Composite Total Particulate and Soot Levels Versus Oxygen Weight Percent in Fuel Without Catalyst.....	56
29 Composite Total Particulate and VOF Levels Versus Volume Percent Biodiesel in Fuel Without Catalyst.....	57

## LIST OF TABLES

<b><u>Table</u></b>	<b><u>Page</u></b>
1 Properties of Test Fuels for Montana DEQ Biodiesel Project.....	4
2 Summary of Conditions Used in Wear Tests.....	11
3 Transient Emissions from a Cummins B5.9L Engine with Rapeseed Biodiesel Fuels.....	13
4 Composition of Particulate Emissions from a Cummins B5..9L Engine with Rapeseed Biodiesel Fuels .....	15
5 Major Constituents of RME and REE Fuels .....	33
6 Compounds Detected and Identified by Mass Spectrography for Cummins B5.9L Engine with Biodiesel Fuels.....	35
7 Composite PAH Levels for Cummins B5.9L Engine with Biodiesel Fuels.....	45
8 Laboratory Scale Wear Test Results.....	53

## EXECUTIVE SUMMARY

Two different biodiesel fuels derived from rapeseed oil were tested at Southwest Research Institute (SwRI) to characterize heavy-duty engine exhaust emissions and biodiesel effects on lubricity. The objective of the program was to compare results for the biodiesel fuels to results obtained with diesel fuel. The two biodiesel fuels were a rapeseed ethyl ester (REE) and a rapeseed methyl ester (RME). Each fuel was tested both neat and in two blend levels, 50 percent and 20 percent by volume with the base diesel fuel. The transient emissions characterization was performed using a 1995 Cummins B5.9L diesel engine, both with and without a catalytic converter (catalyst).

Composite transient emissions data for the four primary pollutants, regulated by the EPA for on-highway engines, is given in the table below. Emissions data are given for all seven test fuels, both with and without catalyst. Transient cycle work and fuel consumption data (BSFC) were also included. In general, the biodiesel fuels reduced transient emissions levels of HC, CO, and total particulate, but had no significant effect on NO<sub>x</sub> levels, as compared to levels obtained with diesel fuel.

### COMPOSITE EMISSIONS FROM A CUMMINS B5.9L ENGINE WITH BIODIESEL FUELS

Fuel	Catalyst	Transient Emissions, g/hp-hr					BSFC, lb/hp-hr	Work, hp-hr
		HC	CO	NO <sub>x</sub>	CO <sub>2</sub>	PM		
2-D	No	0.30	1.47	4.37	609	0.106	0.424	12.5
	Yes	0.25	1.42	4.25	606	0.073	0.422	12.4
REE	No	0.11	0.95	4.26	645	0.091	0.500	11.7
	Yes	0.07	0.64	4.27	651	0.047	0.505	11.7
RME	No	0.09	0.90	4.52	642	0.080	0.498	11.8
	Yes	0.06	0.61	4.48	640	0.042	0.494	11.8
REE50	No	0.17	1.03	4.26	621	0.092	0.458	12.2
	Yes	0.12	0.74	4.37	637	0.058	0.470	12.1
RME50	No	0.16	0.97	4.30	625	0.087	0.460	12.2
	Yes	0.11	0.70	4.30	633	0.055	0.458	12.2
REE20	No	0.23	1.24	4.31	623	0.100	0.444	12.2
	Yes	0.16	0.94	4.30	645	0.067	0.459	12.2
RME20	No	0.22	1.14	4.39	618	0.093	0.444	12.2
	Yes	0.15	0.97	4.33	616	0.064	0.442	12.2

Particulate samples from all transient emission tests were analyzed to determine the composition of the particulate. These data indicated that the reductions observed in particulate emissions when biodiesel fuels were used were due primarily to reduction in the level of carbon soot. Reduced carbon soot probably resulted from improved oxidation of soot in the engine due to the oxygen present in biodiesel. However, the mass of volatile organic material in the particulate, referred to as the volatile organic fraction (VOF), increased when using biodiesel. The net decrease in total particulate using biodiesel fuels would have been larger but the increase in VOF partially offset the reduction in soot. An exhaust catalyst typically reduces the VOF of the particulates. Using biodiesel, the catalyst was able to control the increase in VOF, so that the combined use of biodiesel and a catalyst proved more effective in controlling particulate than either of the two alone. RME had slightly lower levels of regulated emissions than REE.

A disadvantage of the biodiesel fuels was noted in terms of engine performance and fuel economy (BSFC). The engine produced about 6 percent less power when fueled on either of the neat biodiesel fuels, and had significantly higher fuel consumption during the transient cycle. This change was less pronounced with the biodiesel/diesel fuel blends. The performance and fuel economy of the 20 percent blends were nearly identical to that of diesel fuel, whereas the 50 percent blends fell about halfway between the neat biodiesels and diesel fuel. These changes in performance and fuel economy were essentially due to the lower energy content per unit volume of biodiesel as compared to diesel fuel.

Sampling and analysis were also performed on all of the transient tests to try to characterize the compounds present in the gaseous hydrocarbon emissions in more detail. This data indicated that the neat biodiesel fuels appeared to reduce both the total mass and the reactivity, in terms of ozone formation potential, of the gaseous hydrocarbon emissions. It also indicated that the gaseous hydrocarbon emissions associated with using the neat biodiesel fuels were composed of a much narrower range of compounds than was the case for diesel fuel, and that apparently these compounds were more easily oxidized by the catalyst. The results for blended fuels generally followed a pattern similar to that observed for the neat biodiesel fuels, but to a lesser degree as the amount of biodiesel in the blend decreased. The hydrocarbon speciation data for the blends also indicated that the combination of diesel fuel and biodiesel did not produce any unusual toxic compounds not already found in the exhaust of either fuel when run separately.

Detailed analyses of both gaseous and particulate emissions were also made to determine the levels of polycyclic aromatic hydrocarbons (PAH). Gas-phase PAH levels significantly decreased with neat biodiesel fuels as compared to diesel fuel. Some of the particulate-phase PAH compounds also decreased, but several others increased. These same trends were present with the blended fuels, but less strongly than with neat biodiesel fuels. In the case of PAH emissions, the 20 percent blends



gave results essentially identical to the diesel fuel. It should be noted that the mass of gas-phase PAH compounds was several orders of magnitude higher than the mass of particulate-phase PAH compounds. The catalyst appeared to be effective in reducing PAH emissions from all fuels, but it was somewhat more efficient in doing so when the biodiesel fuels were used. The catalyst was also able to control any increases in particulate-phase PAH compounds that occurred when biodiesel was used.

Lubricity testing of the biodiesel fuels was performed on laboratory scale wear testing machines, using two different methods. The test results indicated that both neat RME and REE had excellent lubricating characteristics, superior to any known commercially available diesel fuel. Tests also indicated that blending biodiesel with conventional diesel fuel resulted in a significant improvement in lubricity as compared to the diesel fuel alone.

## I. INTRODUCTION

This final report contains the results of testing conducted at Southwest Research Institute (SwRI) on behalf of the Montana Department of Environmental Quality (DEQ). The work reported herein constitutes Milestones 2 and 3 of a larger DEQ program (contract EDG-93-7549) for which the objective was to characterize engine emissions on two biodiesel fuels derived from rapeseed oil, and to examine the lubricating properties of the two fuels. The two biodiesel fuels examined were a rapeseed methyl ester (RME) and rapeseed ethyl ester (REE). These two fuels were examined in comparison to a typical 2-D diesel fuel, both as neat fuels and as blend components with 2-D diesel fuel.

For Milestone 2, exhaust emissions of a Cummins B5.9L diesel engine were examined using REE and RME, both neat and in blends. Both regulated and unregulated exhaust emissions were characterized, including PAH compounds and hydrocarbon species from C<sub>1</sub> through C<sub>22</sub>. Emissions were measured both with and without a catalytic converter, which was supplied with the engine by Cummins Engine Company. Milestone 3 focused on performing several standard wear tests to evaluate the lubricating properties of both the neat biodiesel fuels and the biodiesel blends for comparison to 2-D diesel fuel.

The primary contact for this program at the DEQ was Howard Haines. Project oversight was provided by Craig Chase, who served as technical consultant for DOE, which provided major funding for this program. Biodiesel test fuels were produced at the University of Idaho, under the supervision of Dr. Chuck Peterson. The test engine and catalyst were provided by Cummins Engine Company. Lead project engineer at SwRI was Christopher Sharp. Most of the chemical analysis, was overseen by Patrick Merritt, except for PAH analysis which was performed by Joseph Pan. Lubricity testing was performed by Paul Lacey.

## II. DESCRIPTION OF PROGRAM

This section of the final report contains a description of the test engine, test fuels, and test procedures used during this program.

### A. Test Engine

The test engine used for this program was a 1995 model year Cummins B5.9L diesel engine. This engine was a four-stroke, six cylinder diesel of in-line configuration, having a displacement of 5.9 liters. The engine was turbocharged and intercooled, and employed a mechanically governed, in-line, fuel injection pump. Engine control input was achieved via a mechanical linkage between the injection pump pedal lever and the test cell servo controller. The engine had a nominal rated maximum power of 160 hp at 2500 rpm, and a nominal peak torque of 400 lb-ft at 1600 rpm. It was supplied with a stock catalytic converter, which was an oxidation catalyst produced by Engelhard. The catalyst was installed in the exhaust, six feet downstream from the turbocharger outlet. Figure 1 shows the engine installed in the transient test cell.

### B. Test Fuels

A total of seven different test fuels were evaluated during this program. Table 1 gives the descriptions of the seven fuels, as well as selected properties of those fuels, as determined by SwRI using standard ASTM test methods. The diesel fuel used during this program, both for baseline emissions testing and as the base fuel for blending, was a 1994 emissions grade, low sulfur, 2-D diesel fuel produced by Phillips Petroleum, Lot No. S-946X, coded SwRI EM-2140-F. The two biodiesel fuels were a rapeseed ethyl ester (REE) and a rapeseed methyl ester (RME), derived from rapeseed oil using transesterification with ethanol and with methanol. Both biodiesels were produced by the University of Idaho.

The blended fuels were produced at SwRI using the following methodology. First, density was measured for all three blend components, 2-D diesel fuel, REE, and RME. These densities were used to determine the correct mass proportions needed to obtain the appropriate volume fraction of each component for the four desired blends. The blends were then produced individually, on a drum-by-drum basis, using a calibrated weigh scale with an accuracy to  $\pm 0.1$  grams. Each drum was then placed on a drum roller for a minimum of one hour, for mixing. The API gravity of each drum mixture was checked against the predicted API gravity, which was based on the volume proportions of the blend recipes and the API gravity of each blend component. The difference between API gravity of each drum of fuel

**FIGURE 1. TRANSIENT TEST CELL INSTALLATION OF THE  
CUMMINS B5.9L ENGINE FOR BIODIESEL TESTING**



and its predicted API gravity was found to be less than 0.2°API in all cases. After the blending was complete, samples of all seven test fuels were pulled for analysis of the properties given in Table 1.

## **C. Test Procedures**

### **1. Transient Testing and Regulated Emissions Measurement**

Emissions were measured over the heavy-duty transient Federal Test Procedure (FTP), following procedures given in CFR Title 40 Part 86, Subpart N. The FTP outlines specific requirements for setting up the test engine and mapping the engine's full torque capabilities over its operating speed range. Engine-specific performance data are used, along with a normalized EPA transient cycle, to define a transient command cycle for test engine operation. The 20 minute transient command cycle illustrated in Figure 2 shows the rapid changes in speed and torque the engine must produce.

While the engine operated over the 20-minute test cycle, torque and speed responses of the engine compared to the command cycle to ensure FTP compliance. Simultaneously, engine exhaust gases are diluted with conditioned air, and emissions of interest are determined. Measured emissions are divided by the level of work performed during the test, and the heavy-duty engine emissions are reported in terms of pollutant mass per unit work.

Emissions measured during this program included total hydrocarbons (THC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), and particulate matter (PM). Hydrocarbons were measured using continuous sampling techniques employing a heated flame ionization detector (HFID). CO and CO<sub>2</sub> were determined using proportional dilute gaseous samples analyzed using non-dispersive infrared (NDIR) instruments. NO<sub>x</sub> was measured continuously during the transient cycle via an NO<sub>x</sub> chemiluminescence instrument. Particulate samples were collected and analyzed to determine the soluble organic fraction (SOF), and the amount of sulfates in the particulate.

Total PM levels were determined by collecting particulate matter on a set of 90mm Pallflex filters, which were weighed both before and after the transient test. Soluble organic fraction (SOF) was determined by analyzing particulate samples collected on the 90mm filters via Soxhlet extraction, using a 30-70 mixture of toluene and ethanol as the solvent. Sulfates were determined by analyzing samples of particulate collected on 47mm Fluoropore filters with an ion chromatograph. Direct filter injection gas chromatography (DFI/GC) applied to a piece of the particulate-laden 90 mm filter was used analyzed to determine volatile organic fraction (VOF) and the contribution of unburned lubricating oil to that VOF.

## **2. Hydrocarbon Speciation**

Detailed speciation analysis was conducted on the hydrocarbon emissions from the cold-start test and the first hot-start test for each day of emissions testing. Two different analyses were conducted, each dealing with a different carbon number range of hydrocarbons. The two ranges examined were C<sub>1</sub> to C<sub>12</sub> hydrocarbons, and C<sub>13</sub> to C<sub>22</sub> hydrocarbons. Each is discussed separately below.

The C<sub>1</sub> to C<sub>12</sub> hydrocarbons were analyzed from the same proportional bag samples of dilute exhaust used to determine CO and CO<sub>2</sub> emissions. Methods for speciating hydrocarbon emissions in this lower carbon number range are well defined, and involve using several gas chromatographs, each set up for a different subset of carbon number range, to quantify levels of about 200 gaseous hydrocarbons. Aldehyde and ketone emissions were determined as part of this process using a DNPH method as described in CFR 40 Part 86 Subpart N for methanol-fueled engines. Each hydrocarbon has been assigned a “maximum

incremental reactivity" (MIR) by CARB. This factor represents the relative reactivity of a given species in generating ozone in the atmosphere, which is a precursor to photochemical smog. Using these MIRs, it is possible to estimate the amount of ozone the total hydrocarbon emissions will generate per unit of work the engine produces.

Identifying heavier hydrocarbons is more difficult, both in terms of sampling and analysis. Beginning with approximately C<sub>13</sub> compounds, the boiling points and vapor pressures of the species are such that they will not remain in the gaseous state unless maintained at elevated temperature. It is not practical to keep gaseous samples at elevated temperatures until analysis, so an alternate sample collection scheme was necessary. Sample collection was accomplished by drawing CVS-diluted exhaust through sorbent tubes packed with a solid sorbent material which has an extremely large surface area. The sorbent tubes are constructed of stainless steel tubing packed with this powdered solid sorbent material, held in place with small end plugs of glass wool and stainless steel screen. The sorbent material used in this project was Tenax GR<sup>®</sup>, useful for capturing hydrocarbons in the mass range of interest. Tenax GR<sup>®</sup> is also hydrophobic, so it is a good choice for sampling exhaust, which is very humid. Excess water can be a problem with some sorbents because preferential adsorption of water can displace sample molecules. Molecules making up the sample adsorb on the Tenax GR<sup>®</sup> at ambient temperatures, and can be subsequently desorbed by heating the sorbent material.

The sampling system is depicted in Figure 3. Exhaust samples were collected continuously during the test cycle. The temperature of the sampling system up to the sorbent tubes is maintained at 375°F to prevent condensation of analyte molecules. Before reaching the sorbent tubes, the sample passes through heated, flip-top filter holders fitted with glass fiber particulate filters.

For analysis, samples are thermally desorbed onto a 60m long x 0.32 mm diameter, 1µm film DB-1 gas chromatograph column coupled to a quadrupole mass spectrometer (GC/MS). A thermal desorption autosampler is used to heat the sorbent tube to 300°C while the inert carrier gas, helium, purges the sample from the tube. The sample tube is purged onto a cold trap for 20 minutes where the sample is subsequently caught on a cold trap maintained at 0°C. At this point the cold trap is ballistically heated to 300°C, introducing the sample onto the GC column all at one time. The mass spectrometer is operated in full scan mode, resulting in spectra that can be compared to a database of over 138,000 reference spectra. A computer algorithm is used to rapidly compare the unknown spectra against those in the database, and to rank them on the degree of fit. A chemist may then make a final determination as to the unknown compound's identity.



Because the mass spectrometric analysis of the components of diesel exhaust is not well developed, the information gained from this work is largely qualitative. Any quantitative information is limited to discussion of relative amounts in a particular sample. This limitation stems from the fact that to accurately quantify particular compounds, one must have pure samples of the compound on hand to make up quantitative reference standards. Such effort was beyond the scope of this research.

### **3. PAH Analysis**

Polycyclic aromatic hydrocarbons (PAH) were sampled using both a polyurethane foam (PUF) and a 20×20-inch Pallflex filter. This was done to insure collection of both gas phase and particulate phase PAH compounds. Details of the sampling and analysis of both media are given below.

Polyurethane filters (PUFs) were prepared for sample collection by extracting them with acetone for 24 hours, hexane for 48 hours, and then acetone again for 24 hours. The cleaned PUF is then blown dry under nitrogen for 12 to 15 hours. One hundred  $\mu\text{L}$  of a surrogate solution containing fluorene-d10, fluoranthene-d10, and pyrene-d10 at a level of 20 ng/ $\mu\text{L}$  was spiked to both the PUF and filter media following cleanup to monitor collection efficiency. The concentration at final volume was 2.0 ng/ $\mu\text{L}$ .

Exposed PUF and filter media were stored at 4°C following sampling and prior to extraction. The holding period did not exceed 4 days. PUF media were extracted with hexane:diethyl ether (94:6) by continuous Soxhlet extraction for 16 to 20 hours. Filter media were extracted with toluene by Soxhlet continuous extraction for 18 hrs. Solvents used were ultra high purity Fisher Optima<sup>®</sup> quality. One hundred  $\mu\text{L}$  of a surrogate solution containing 4,4'-dibromobiphenyl, anthracene-d10, and p-terphenyl-d14 at a level of 20 ng/ $\mu\text{L}$  was spiked to the media just prior to extraction, to monitor extraction efficiency. The concentration at final volume was 2.0 ng/ $\mu\text{L}$ .

Extracts were concentrated by transferring to Kuderna-Danish apparatus and heating over a steam bath to a volume of several mL. Quantitative transfer of the extract to vials followed, then further concentration with a stream of nitrogen until a final volume of 1 mL was reached. Sample extracts were stored at 4°C. Matrix spike analyses were made by spiking a blank sample (solvent only) with a solution of all target analytes, at a mid-level concentration of 1 ng/ $\mu\text{L}$  in the final extract, and treated in the same manner as the sampling media.

No cleanup procedures were performed on the sample extracts. PUF extracts were sufficiently clean that a cleanup step was not needed. Filter extracts contained some debris and would have possibly benefitted from a cleanup step; although analysis at a 10-fold dilution appeared to resolve most interference issues, and was required in most cases to reduce the level of analytes to the calibrated range of the MS.

GC/MS analysis was performed on a quadrupole instrument operated in selected ion monitoring (SIR) mode. Separation of PAHs was accomplished by injecting a 1  $\mu\text{L}$  aliquot of the sample extract onto a 60 m DB-5 capillary column. For quantitation, an internal standard solution, made up of several deuterated PAHs, was spiked into the extract at the time of analysis and was used for calculating response factors. A linearity criterion of 30% RSD was used for a multi-point calibration curve established over the range from 0.01 to 10 ng/ $\mu\text{L}$  (0.01 to 10 total  $\mu\text{g}/\text{sample}$ ).

PUF extracts were analyzed without dilution, whereas most filter extracts were sufficiently concentrated or high in PAHs that a 10-fold dilution was needed. While the established quantitation limit was 0.01  $\mu\text{g}/\text{sample}$ , the sensitivity in SIR mode improved the lower detection limit by a factor of five for all PAHs, with the exception of nitropyrene.

#### **4. Lubricity Testing**

Laboratory scale wear tests were performed using two different experimental methods, the High Frequency Reciprocating Rig (HFRR) and the

Scuffing Load Ball on Cylinder Lubricity Evaluator (SLBOCLE). Each of these two test procedures is described below.

The SLBOCLE determines the minimum applied load required for a step transition to adhesive scuffing. During testing, the fluid is placed in a humidity-controlled chamber. A non-rotating steel ball is held in a vertically mounted chuck and forced against an axially mounted polished steel ring. A sequence of one-minute tests is done, and the applied load is systematically changed until a disproportionate change in friction and wear is observed. The fuel is not renewed between load increments during a normal test sequence. The test cylinder is rotated at a fixed speed while being partially immersed in the fluid reservoir. This partial immersion maintains the cylinder in a wet condition and continuously transports the test fluid to the ball/cylinder interface. The minimum applied load required to produce a transition from sliding contact to severe friction and wear is a measure of the fluid-lubricating properties and this load is inversely related to wear.

The HFRR apparatus uses an electromagnetic vibrator to oscillate a moving specimen over a small amplitude while pressed against a fixed specimen. The fixed specimen is held in a small bath, which contains the test fuel. Bath temperature is controlled. The wear scar formed on the fixed specimen is measured and used to assess the lubricity of the test fuel. Provision is also made to measure the friction force transmitted between the two test specimens.

The conditions used for the wear tests in the present study are summarized in Table 2. Results obtained from both the SLBOCLE and HFRR test procedures show directional correlation with full scale equipment. For the SLBOCLE test, a minimum applied load more than 3,000 grams shows that, on average, a fuel is likely to produce acceptable wear in full-scale equipment. For the HFRR, a wear scar diameter of less than 0.38 mm indicates an acceptable fuel. However, both these values are unlikely to be absolute, and will vary as a function of fuel viscosity, operating temperature, and individual equipment requirements. As a result, most organizations have adopted different minimum fuel lubricity requirements, based on the application and the margin of safety needed.

**TABLE 2. SUMMARY OF CONDITIONS USED IN WEAR TESTS**

Variable	SLBOCLE	HFRR
App. Load, kg	0.5–8.0	0.2
Speed, rpm Oscillation, Hz	525	50
Duration, min.	1	75
Break In, sec.	30	None
Atmosphere	Controlled Air	Uncontrolled
Humidity, %Rh	50	Ambient
Temperature, °C	25	Ambient
Pass/Fail*	3.0 kg	0.38mm
*Tentative Value		

### III. TEST RESULTS

This section of the report discusses results of the program in detail. It is broken down into sections to focus on individual areas of test results, including regulated transient emissions, hydrocarbon speciation, PAH analysis, and lubricity testing.

#### A. Regulated Transient Emissions

This section presents the regulated emission results measured during transient testing of the Cummins B5.9L engine using all seven test fuels. It also includes the effect of the various fuels on the performance and fuel consumption of the engine. In addition, the results of DFI/GC, SOF, and sulfate analyses of particulate matter are also presented in this section. No smoke testing was performed during this program.

##### 1. **Base 2-D Diesel Fuel**

The results of all transient tests are summarized in Table 3 for regulated emissions and CO<sub>2</sub>, and Table 4 for particulate composition results. Detailed printouts of individual transient tests are given in Appendix A. Composite regulated emissions without catalyst for all seven fuels are depicted in Figure 4. The composition of particulate emissions is given in Figure 5 for all tests without the catalyst. Figure 6 shows the effects of the biodiesel fuels in terms of the percent reduction in emissions observed compared to 2-D fuel, without catalyst. Composite regulated emissions with the catalyst for all fuels are shown in Figure 7. Particulate composition for tests with the catalyst are shown in Figure 8. Figure 9 shows a comparison of biodiesel fuels to diesel fuel in percent difference with the catalyst installed. Figure 10 shows average transient torque-map data for all seven fuels.

Transient testing of the Cummins B 5.9L engine commenced on October 31, 1995 with the 2-D diesel fuel. Initial tests using 2-D fuel indicated that the engine was operating as expected. Regulated emission levels were very close to those posted by Cummins for this engine. Particulate matter with 2-D fuel was composed of about 53 percent soot and about 40 percent volatile organics(VOF). About half the organics were unburned lube oil, the rest being primarily unburned fuel. Sulfates and bound water made up only about 7 percent of the total particulate matter.

**TABLE 3. TRANSIENT EMISSIONS FROM A CUMMINS  
B5.9L ENGINE WITH RAPESEED BIODIESEL FUELS**

Test Number	Fuel	Catalyst	Transient Emissions (g/hp-hr)					BSFC, lb/hp-hr	Work, hp-hr
			HC	CO	NOx	CO <sub>2</sub>	PM		
Cummins	Baseline	Yes	0.21	1.30	4.05	577	0.079	--	--
A-C1	2-D	No	0.39	1.92	4.52	612	0.123	0.427	12.7
A-H1	2-D	No	0.28	1.40	4.33	601	0.104	0.418	12.6
A-H2	2-D	No	0.29	1.39	4.36	615	0.103	0.428	12.4
<b>Composite</b>	<b>2-D</b>	<b>No</b>	<b>0.30</b>	<b>1.47</b>	<b>4.37</b>	<b>609</b>	<b>0.106</b>	<b>0.424</b>	<b>12.5</b>
AC-C1	2-D	Yes	0.33	2.03	4.46	619	0.078	0.432	12.6
AC-H1	2-D	Yes	0.25	1.32	4.22	608	0.071	0.423	12.4
AC-H2	2-D	Yes	0.23	1.30	4.21	600	0.073	0.417	12.4
<b>Composite</b>	<b>2-D</b>	<b>Yes</b>	<b>0.25</b>	<b>1.42</b>	<b>4.25</b>	<b>606</b>	<b>0.073</b>	<b>0.422</b>	<b>12.4</b>
A-C3	2-D	No	0.36	2.02	4.61	644	0.120	0.449	12.3
A-H4	2-D	No	0.29	1.46	4.36	636	0.103	0.442	12.2
A-H5	2-D	No	0.30	1.48	4.38	632	0.106	0.440	12.2
<b>Composite</b>	<b>2-D</b>	<b>No</b>	<b>0.30</b>	<b>1.55</b>	<b>4.40</b>	<b>635</b>	<b>0.107</b>	<b>0.442</b>	<b>12.2</b>
B-C1	REE	No	0.15	1.16	4.33	666	0.106	0.517	11.8
B-H1	REE	No	0.11	0.88	4.25	643	0.008	0.499	11.8
B-H2	REE	No	0.11	0.96	4.26	639	0.089	0.496	11.7
<b>Composite</b>	<b>REE</b>	<b>No</b>	<b>0.11</b>	<b>0.95</b>	<b>4.26</b>	<b>645</b>	<b>0.091</b>	<b>0.500</b>	<b>11.7</b>
BC-C1	REE	Yes	0.10	0.89	4.33	670	0.055	0.520	11.7
BC-H1	REE	Yes	0.06	0.59	4.25	649	0.045	0.503	11.7
BC-H2	REE	Yes	0.07	0.61	4.26	647	0.046	0.501	11.6
<b>Composite</b>	<b>REE</b>	<b>Yes</b>	<b>0.07</b>	<b>0.64</b>	<b>4.26</b>	<b>651</b>	<b>0.047</b>	<b>0.505</b>	<b>11.7</b>
B-C2	REE	No	0.19	1.41	4.44	663	0.113	0.516	11.4
B-H3	REE	No	0.10	1.02	4.37	648	0.087	0.504	11.5
B-H4	REE	No	0.10	1.00	4.45	648	0.090	0.503	11.4
<b>Composite</b>	<b>REE</b>	<b>No</b>	<b>0.11</b>	<b>1.06</b>	<b>4.41</b>	<b>650</b>	<b>0.092</b>	<b>0.505</b>	<b>11.4</b>
C-C1	RME	No	0.12	1.17	4.59	655	0.096	0.509	11.8
C-H1	RME	No	0.08	0.84	4.53	637	0.077	0.494	11.8
C-H2	RME	No	0.08	0.88	4.50	643	0.078	0.499	11.8
<b>Composite</b>	<b>RME</b>	<b>No</b>	<b>0.09</b>	<b>0.90</b>	<b>4.52</b>	<b>642</b>	<b>0.080</b>	<b>0.498</b>	<b>11.8</b>
CC-C1	RME	Yes	0.10	0.89	4.51	648	0.052	0.500	11.9
CC-H1	RME	Yes	0.05	0.57	4.47	633	0.042	0.488	11.9
CC-H2	RME	Yes	0.06	0.56	4.48	645	0.040	0.497	11.8

<b>Composite</b>	<b>RME</b>	<b>Yes</b>	<b>0.06</b>	<b>0.61</b>	<b>4.48</b>	<b>640</b>	<b>0.042</b>	<b>0.494</b>	<b>11.8</b>
------------------	------------	------------	-------------	-------------	-------------	------------	--------------	--------------	-------------

**TABLE 3 (CONT'D). TRANSIENT EMISSIONS FROM A  
CUMMINS B5.9L ENGINE WITH RAPESEED BIODIESEL FUELS**

Test Number	Fuel	Catalyst	Transient Emissions (g/hp-hr)					BSFC, lb/hp-hr	Work, hp-hr
			HC	CO	NOx	CO <sub>2</sub>	PM		
D-C1	REE50	No	0.20	1.33	4.39	651	0.100	0.480	0.480
D-H1	REE50	No	0.16	0.99	4.20	618	0.091	0.456	0.456
D-H2	REE50	No	0.16	0.98	4.26	615	0.090	0.453	0.453
<b>Composite</b>	<b>REE50</b>	<b>No</b>	<b>0.17</b>	<b>1.03</b>	<b>4.25</b>	<b>621</b>	<b>0.092</b>	<b>0.458</b>	<b>0.458</b>
DC-C1	REE50	Yes	0.16	1.02	4.47	642	0.064	0.473	12.0
DC-H1	REE50	Yes	0.11	0.66	4.38	638	0.057	0.470	12.1
DC-H2	REE50	Yes	0.12	0.73	4.32	635	0.057	0.468	12.1
<b>Composite</b>	<b>REE50</b>	<b>Yes</b>	<b>0.12</b>	<b>0.74</b>	<b>4.37</b>	<b>637</b>	<b>0.058</b>	<b>0.470</b>	<b>12.1</b>
E-C1	RME50	No	0.19	1.20	4.46	630	0.094	0.463	12.3
E-H1	RME50	No	0.15	0.91	4.28	626	0.087	0.460	12.2
E-H2	RME50	No	0.15	0.96	4.27	623	0.085	0.458	12.2
<b>Composite</b>	<b>RME50</b>	<b>No</b>	<b>0.16</b>	<b>0.97</b>	<b>4.30</b>	<b>625</b>	<b>0.087</b>	<b>0.460</b>	<b>12.2</b>
EC-C1	RME50	Yes	0.14	0.97	4.44	637	0.059	0.468	12.2
EC-H1	RME50	Yes	0.11	0.64	4.29	623	0.055	0.458	12.2
EC-H2	RME50	Yes	0.11	0.67	4.27	619	0.054	0.454	12.2
<b>Composite</b>	<b>RME50</b>	<b>Yes</b>	<b>0.11</b>	<b>0.70</b>	<b>4.30</b>	<b>623</b>	<b>0.055</b>	<b>0.458</b>	<b>12.2</b>
F-C1	REE20	No	0.28	1.66	4.45	634	0.112	0.452	12.3
F-H1	REE20	No	0.22	1.17	4.27	619	0.097	0.441	12.2
F-H2	REE20	No	0.22	1.17	4.30	624	0.098	0.444	12.2
<b>Composite</b>	<b>REE20</b>	<b>No</b>	<b>0.23</b>	<b>1.24</b>	<b>4.31</b>	<b>623</b>	<b>0.100</b>	<b>0.444</b>	<b>12.2</b>
FC-C1	REE20	Yes	0.20	1.29	4.45	644	0.071	0.459	12.3
FC-H1	REE20	Yes	0.16	0.85	4.29	641	0.065	0.456	12.2
FC-H2	REE20	Yes	0.15	0.91	4.25	650	0.067	0.463	12.2
<b>Composite</b>	<b>REE20</b>	<b>Yes</b>	<b>0.16</b>	<b>0.94</b>	<b>4.30</b>	<b>645</b>	<b>0.067</b>	<b>0.459</b>	<b>12.2</b>
G-C1	RME20	No	0.25	1.43	4.57	626	0.101	0.450	12.3
G-H1	RME20	No	0.21	1.07	4.37	611	0.089	0.438	12.2
G-H2	RME20	No	0.21	1.11	4.35	623	0.095	0.447	12.2
<b>Composite</b>	<b>RME20</b>	<b>No</b>	<b>0.22</b>	<b>1.14</b>	<b>4.39</b>	<b>618</b>	<b>0.093</b>	<b>0.444</b>	<b>12.2</b>
GC-C1	RME20	Yes	0.18	1.29	4.45	626	0.073	0.450	12.3
GC-H1	RME20	Yes	0.14	0.89	4.35	613	0.062	0.439	12.2
GC-H2	RME20	Yes	0.15	0.94	4.28	616	0.063	0.442	12.2
<b>Composite</b>	<b>RME20</b>	<b>Yes</b>	<b>0.15</b>	<b>0.97</b>	<b>4.33</b>	<b>616</b>	<b>0.064</b>	<b>0.442</b>	<b>12.2</b>



**TABLE 4. COMPOSITION OF PARTICULATE EMISSIONS FROM  
A CUMMINS B5.9L ENGINE WITH RAPESEED BIODIESEL FUELS**

Test Number	Fuel	Catalyst	VOF - DFI/GC			SOF-Soxhlet		Sulfate		Soot, <sup>a</sup> g/hp-hr	
			%	g/hp-hr	%oil	%	g/hp-hr	%	g/hp-hr	w/DFI	w/SOF
A-C1	2-D	No	36	0.045	57	57	0.07	2.7	0.003	0.070	0.04
A-H1	2-D	No	37	0.038	51	47	0.05	2.8	0.003	0.059	0.05
A-H2	2-D	No	38	0.040	52	47	0.05	2.6	0.003	0.056	0.05
<b>Composite</b>	<b>2-D</b>	<b>No</b>	<b>37</b>	<b>0.040</b>	<b>53</b>	<b>48</b>	<b>0.05</b>	<b>2.7</b>	<b>0.003</b>	<b>0.059</b>	<b>0.05</b>
A-C1	2-D	Yes	32	0.025	47	36	0.03	1.1	0.001	0.051	0.05
A-H1	2-D	Yes	25	0.018	40	20	0.01	1.1	0.001	0.051	0.05
A-H2	2-D	Yes	32	0.024	50	35	0.03	0.9	0.001	0.047	0.05
<b>Composite</b>	<b>2-D</b>	<b>Yes</b>	<b>29</b>	<b>0.022</b>	<b>45</b>	<b>29</b>	<b>0.02</b>	<b>1.0</b>	<b>0.001</b>	<b>0.049</b>	<b>0.05</b>
A-C2	2-D	No	37	0.045	62	48	0.06	2.5	0.003	0.068	0.05
A-H3	2-D	No	38	0.039	48	40	0.04	2.5	0.003	0.058	0.06
A-H4	2-D	No	39	0.042	60	47	0.05	2.5	0.003	0.057	0.05
<b>Composite</b>	<b>2-D</b>	<b>No</b>	<b>38</b>	<b>0.041</b>	<b>55</b>	<b>44</b>	<b>0.05</b>	<b>2.5</b>	<b>0.003</b>	<b>0.059</b>	<b>0.05</b>
B-C1	REE	Yes	72	0.076	60	53	0.06	0.3	0.000	0.029	0.05
B-H1	REE	Yes	61	0.053	41	54	0.05	0.4	0.000	0.034	0.04
B-H2	REE	Yes	64	0.057	48	64	0.06	0.2	0.000	0.032	0.03
<b>Composite</b>	<b>REE</b>	<b>Yes</b>	<b>64</b>	<b>0.058</b>	<b>47</b>	<b>58</b>	<b>0.05</b>	<b>0.3</b>	<b>0.000</b>	<b>0.032</b>	<b>0.04</b>
B-C1	REE	No	42	0.023	44	57	0.03	0.4	0.000	0.031	0.02
B-H1	REE	No	42	0.019	33	47	0.02	0.6	0.000	0.025	0.02
B-H2	REE	No	48	0.022	39	56	0.03	0.5	0.000	0.023	0.02
<b>Composite</b>	<b>REE</b>	<b>No</b>	<b>45</b>	<b>0.021</b>	<b>37</b>	<b>52</b>	<b>0.02</b>	<b>0.5</b>	<b>0.000</b>	<b>0.025</b>	<b>0.02</b>
B-C2	REE	Yes	63	0.071	48	75	0.08	0.2	0.000	0.041	0.03
B-H3	REE	Yes	62	0.054	38	82	0.07	0.3	0.000	0.032	0.02
B-H4	REE	Yes	68	0.061	47	71	0.06	0.3	0.000	0.028	0.03
<b>Composite</b>	<b>REE</b>	<b>Yes</b>	<b>65</b>	<b>0.069</b>	<b>43</b>	<b>76</b>	<b>0.07</b>	<b>0.3</b>	<b>0.000</b>	<b>0.032</b>	<b>0.02</b>
C-C1	RME	No	23	0.022	45	70	0.07	0.3	0.000	0.073	0.03
C-H1	RME	No	63	0.049	37	76	0.06	0.3	0.000	0.027	0.02
C-H2	RME	No	25	0.078	40	74	0.06	0.3	0.000	0.000	0.02
<b>Composite</b>	<b>RME</b>	<b>No</b>	<b>41</b>	<b>0.058</b>	<b>39</b>	<b>74</b>	<b>0.06</b>	<b>0.3</b>	<b>0.000</b>	<b>0.022</b>	<b>0.02</b>
C-C1	RME	Yes	102	0.053	52	61	0.03	0.4	0.000	0.000	0.02
C-H1	RME	Yes	53	0.022	41	65	0.03	0.6	0.000	0.018	0.01
C-H2	RME	Yes	115	0.036	52	62	0.02	0.5	0.000	0.000	0.01

<b>Composite</b>	<b>RME</b>	<b>Yes</b>	<b>87</b>	<b>0.037</b>	<b>47</b>	<b>63</b>	<b>0.03</b>	<b>0.5</b>	<b>0.000</b>	<b>0.005</b>	<b>0.02</b>
<sup>a</sup> Soot w/DFI is calculated using VOF by DFI-GC and w/SOF is calculated using SOF by Soxhlet extraction.											

**TABLE 4 (CONT'D). COMPOSITION OF PARTICULATE EMISSIONS FROM  
A CUMMINS B5.9L ENGINE WITH RAPESEED BIODIESEL FUELS**

Test Number	Fuel	Catalyst	VOF - DFI/GC			SOF-Soxhlet		Sulfate		Soot, <sup>a</sup> g/hp-hr	
			%	g/hp-hr	%oil	%	g/hp-hr	%	g/hp-hr	w/DFI	w/SOF
D-C2	REE50	No	26	0.026	41	65	0.07	1.6	0.002	0.070	0.03
D-H1	REE50	No	46	0.042	46	61	0.06	1.6	0.001	0.045	0.03
D-H2	REE50	No	31	0.028	41	62	0.06	1.5	0.001	0.059	0.03
<b>Composite</b>	<b>REE50</b>	<b>No</b>	<b>37</b>	<b>0.034</b>	<b>43</b>	<b>62</b>	<b>0.06</b>	<b>1.6</b>	<b>0.001</b>	<b>0.055</b>	<b>0.03</b>
DC-C1	REE50	Yes	100	0.064	50	41	0.03	1.1	0.001	0.000	0.04
DC-H1	REE50	Yes	34	0.019	43	37	0.02	1.1	0.001	0.036	0.03
DC-H2	REE50	Yes	51	0.029	47	42	0.02	1.2	0.001	0.026	0.03
<b>Composite</b>	<b>REE50</b>	<b>Yes</b>	<b>51</b>	<b>0.030</b>	<b>46</b>	<b>40</b>	<b>0.02</b>	<b>1.1</b>	<b>0.001</b>	<b>0.027</b>	<b>0.03</b>
E-C1	RME50	No	53	0.049	57	62	0.06	1.8	0.002	0.041	0.03
E-H1	RME50	No	54	0.047	60	63	0.05	1.6	0.001	0.037	0.03
E-H2	RME50	No	55	0.047	53	66	0.06	1.6	0.001	0.035	0.03
<b>Composite</b>	<b>RME50</b>	<b>No</b>	<b>54</b>	<b>0.047</b>	<b>57</b>	<b>64</b>	<b>0.06</b>	<b>1.6</b>	<b>0.001</b>	<b>0.036</b>	<b>0.03</b>
EC-C1	RME50	Yes	38	0.023	44	52	0.03	1.9	0.001	0.033	0.03
EC-H1	RME50	Yes	43	0.024	50	45	0.02	1.5	0.001	0.029	0.03
EC-H2	RME50	Yes	37	0.020	45	46	0.02	1.8	0.001	0.032	0.03
<b>Composite</b>	<b>RME50</b>	<b>Yes</b>	<b>40</b>	<b>0.022</b>	<b>47</b>	<b>46</b>	<b>0.03</b>	<b>1.7</b>	<b>0.001</b>	<b>0.031</b>	<b>0.03</b>
F-C1	REE20	No	33	0.037	63	65	0.07	2.2	0.002	0.069	0.03
F-H1	REE20	No	48	0.046	60	58	0.06	1.9	0.002	0.046	0.04
F-H2	REE20	No	45	0.044	54	60	0.06	2.2	0.002	0.049	0.03
<b>Composite</b>	<b>REE20</b>	<b>No</b>	<b>45</b>	<b>0.044</b>	<b>58</b>	<b>60</b>	<b>0.06</b>	<b>2.1</b>	<b>0.002</b>	<b>0.051</b>	<b>0.03</b>
FC-C1	REE20	Yes	29	0.021	49	48	0.03	1.6	0.001	0.047	0.03
FC-H1	REE20	Yes	29	0.019	52	37	0.02	1.6	0.001	0.043	0.04
FC-H2	REE20	Yes	29	0.019	44	35	0.02	1.7	0.001	0.045	0.04
<b>Composite</b>	<b>REE20</b>	<b>Yes</b>	<b>29</b>	<b>0.019</b>	<b>48</b>	<b>38</b>	<b>0.03</b>	<b>1.6</b>	<b>0.001</b>	<b>0.045</b>	<b>0.04</b>
G-C1	RME20	No	47	0.048	59	61	0.06	2.3	0.002	0.047	0.03
G-H1	RME20	No	44	0.039	47	56	0.05	2.7	0.002	0.044	0.03
G-H2	RME20	No	44	0.041	58	60	0.06	2.5	0.002	0.048	0.03
<b>Composite</b>	<b>RME20</b>	<b>No</b>	<b>44</b>	<b>0.041</b>	<b>53</b>	<b>58</b>	<b>0.05</b>	<b>2.6</b>	<b>0.002</b>	<b>0.048</b>	<b>0.03</b>
GC-C1	RME20	Yes	15	0.011	51	29	0.02	1.4	0.001	0.059	0.05

GC-H1	RME20	Yes	33	0.020	37	34	0.02	1.5	0.001	0.040	0.04
GC-H2	RME20	Yes	30	0.019	43	31	0.02	1.4	0.001	0.042	0.04
<b>Composite</b>	<b>RME20</b>	<b>Yes</b>	<b>29</b>	<b>0.018</b>	<b>42</b>	<b>32</b>	<b>0.02</b>	<b>1.4</b>	<b>0.001</b>	<b>0.043</b>	<b>0.04</b>
<sup>a</sup> Soot w/DFI is calculated using VOF by DFI-GC and w/SOF is calculated using SOF by Soxhlet extraction.											















A repeat test day was run with 2-D fuel to address the question of day-to-day repeatability. Both the regulated emissions and the particulate composition were repeated, generally within one percent, except for CO and BSFC which had slightly higher variation.

When the catalyst was installed, no changes in engine performance or fuel economy were observed. With the catalyst, which is the typical configuration for this engine, the composite regulated emissions of the engine on 2-D fuel were well within the 1995 emissions standards for on-road heavy-duty diesel engines. The catalyst reduced hydrocarbon emissions by 16 percent, and reduced total particulate emissions by 31 percent. The catalyst had no effect on NO<sub>x</sub> emissions, as expected, but it was also ineffective in reducing CO.

Particulate composition results, given in Figure 8, indicate that the catalyst was very effective in reducing the unburned fuel and oil portions of the particulate by about 50 percent each, but that it had essentially no effect on the other constituents of the particulate matter. The low HC oxidation efficiency of the catalyst, compared to reasonable particulate oxidation, indicated that this catalyst was very effective in oxidizing heavier hydrocarbons, but not very efficient at oxidizing light hydrocarbons. This observation was confirmed by the hydrocarbon speciation data, as discussed later, and it was later learned that this particular oxidation catalyst was primarily designed to control particulate emissions by oxidizing heavier organic hydrocarbons, such as unburned diesel fuel and oil. The catalyst was not very effective on CO and lighter hydrocarbon emissions.

## **2. Neat Biodiesel Fuels**

Both neat biodiesel fuels, REE and RME, had a significant effect on engine performance and brake specific fuel consumption (BSFC). Both neat biodiesel fuels resulted in a loss of performance, as reflected by an average of 6 percent less torque over the transient torque-map, as well as a reduction in work done during the transient cycle. BSFC was also poorer with REE and RME. Transient cycle BSFC increased as much as 18 percent over 2-D fuel. These results are consistent with the lower energy content of biodiesel relative to diesel fuel, although the increase in BSFC was larger than expected based on energy content alone. RME had a slightly smaller performance and BSFC penalty than REE.

As shown in Figure 6, compared to 2-D fuel, HC emissions were 62 and 72 percent lower for REE and RME, respectively. Lower HC emissions are probably due in part to the oxygen in the biodiesel fuel, but also due to the fact that unburned biodiesel is composed of heavy (C<sub>18</sub> to C<sub>20</sub>) compounds with high boiling points, and contains no light- and middle-distillate hydrocarbon components as diesel fuel does. Therefore unburned biodiesel will likely condense to form particulate matter. CO emissions were roughly 40 percent lower with both neat

biodiesel fuels, probably a result of the high oxygen content of neat biodiesel. Compared to 2-D, NO<sub>x</sub> did not show any significant change with REE, while RME appeared to cause a slight increase in NO<sub>x</sub>. Particulate emissions using REE and RME were 14 and 25 percent lower than obtained on 2-D fuel.

Examination of the particulate composition data in Figure 5 shows that soot decreased 50 percent or more for both REE and RME, likely as a result of the fuels' high oxygen content. Particulate from RME had slightly lower soot levels than REE. However, the volatile organic fraction of particulates derived from unburned fuel was roughly 50 percent higher with neat biodiesel than with 2-D fuel because unburned biodiesel fuel tends to be measured as particulate matter, rather than as gaseous hydrocarbons. The sulfate portion of the total particulate was essentially eliminated with neat biodiesel because biodiesel contains no sulfur, although this had a very small impact on total particulate emission levels.

Comparing results shown in Figure 6 and Figure 9, the percent differences in HC, CO, and particulate with the neat biodiesel fuels compared to diesel fuel were larger with the catalyst than without the catalyst. Another way to examine this is to look at the conversion efficiency of the catalyst for both biodiesel and diesel fuel. Figure 11 shows the conversion efficiency of the catalyst on each of the regulated pollutants for all seven fuels. For both REE and RME, the conversion efficiency of the catalyst was higher on HC, CO, and particulate than it is for 2-D fuel. This means that biodiesel produced less of these pollutants in the engine exhaust, and also enhanced the ability of the catalyst to reduce the engine-out emissions.

In the case of particulates, the improved conversion efficiency of the catalyst with biodiesel fuel can perhaps be explained by the fact that volatile organic compounds made up a much larger fraction of the total particulates with neat biodiesel fuel than with diesel fuel. Because this catalyst was most effective on this portion of particulates, it would tend to be more efficient in reducing particulates from a biodiesel-fueled engine. The data shown in Figure 8 indicate that the catalyst had no difficulty in dealing with the increased volatile organics emitted from the biodiesel fueled engine, and the soot levels were also reduced due to the oxygen in the biodiesel. For HC and CO emissions, the increased catalyst efficiency is difficult to explain. A more detailed study would be required to determine the exact mechanism at work.



### **3. 50 Percent Biodiesel Blends**

The two 50 percent diesel and biodiesel blends, REE50 and RME50, did not have nearly the same adverse impact on performance and BSFC as the neat biodiesel fuels. There was still a loss in torque of about 3 percent over the torque-map, and a similar loss of work over the transient cycle. Transient cycle BSFC was about 8 percent higher on the 50 percent blends compared to diesel fuel. This reflects the fact that the 50 percent blends fall about halfway between the neat biodiesels and diesel fuel in terms of energy content.

In terms of regulated emissions, the levels observed for CO and particulates with the 50 percent biodiesel blends were nearly the same as for the neat biodiesel fuel. Decreases from 2-D fuel hydrocarbon levels with REE50 and RME50 were smaller than with REE and RME, but they were still about 50 percent lower. As before, the methyl ester blend (RME50) achieved slightly lower levels of HC, CO, and particulate than the ethyl ester blend (REE50). NO<sub>x</sub> emission levels observed with diesel fuel were unchanged with the 50 percent blends. Particulate composition data with REE50 and RME50 showed that carbon soot was reduced compared to 2-D fuel, but unburned fuel-derived VOF increased, although not quite as much as was the case for REE and RME. This indicated that the trends in particulate composition observed with neat biodiesel were similar with the 50 percent blends, but to a slightly lower degree. This reflects the fact that there tends to be less unburned biodiesel with the 50 percent blends, as compared to the neat biodiesel, but also about half as much oxygen in the blends as in the neat biodiesel fuels. Sulfate levels were about half the level observed for diesel fuel.

Catalyst oxidation efficiency for HC and CO with the 50 percent blends was significantly better than with diesel fuel, and nearly as good as it had been for the neat biodiesel fuels. However, particulate conversion efficiency was lower with REE50 and RME50 than with REE and RME. This lower catalyst efficiency with the 50 percent blends reflects the smaller fraction of particulates made up of VOF with the 50 percent blends than when the neat biodiesel fuels were tested.

### **4. 20 Percent Biodiesel Blends**

The 20 percent blends, REE20 and RME20, had no appreciable effect on engine performance, and only a small effect on BSFC. Torque levels with the 20 percent blends were nearly identical to those obtained with 2-D fuel, as was transient cycle work. BSFC with the 20 percent blends was about 5 percent worse than for diesel fuel.

Regulated emission data indicated that significant reductions in HC and CO emissions were evident with REE20 and RME20, as compared to 2-D fuel. However, particulates were only about 10 percent lower. NO<sub>x</sub> emissions remained unchanged. Particulate composition data for the 20 percent blends indicated lower

levels of soot and increased VOF, compared to 2-D fuel, but these variations were fairly small, and sulfates were nearly identical to the levels observed for diesel fuel. With the 20 percent blends the trends in particulate composition are consistent with those for the higher biodiesel content fuels, but the levels of change were much smaller. As had been observed for the neat biodiesel and the 50 percent blends, the methyl ester appeared to reduce HC, CO, and particulate emissions slightly better than the ethyl ester.

Catalyst efficiency in reducing HC and CO emissions remained significantly higher with REE20 and RME20 than for 2-D fuel. Apparently the mechanism of enhanced conversion of HC and CO depends more on the presence of some threshold quantity of biodiesel, rather than on the gross amount of biodiesel present. Particulate conversion efficiency was identical to that observed for 2-D fuel, and reflects similar particulate compositions for the 20 percent blends and the diesel fuel.

## **B. Hydrocarbon Speciation**

### **1. $C_1$ - $C_{12}$ Speciation**

Speciation data for hydrocarbons in the  $C_1$  -  $C_{12}$  range is given in Appendix B. These data are also shown graphically in Appendix C, which summarizes the composite data for each fuel by carbon number and general class of compounds, both in terms of mass and ozone formation potential.

The  $C_1$  -  $C_{12}$  speciation data for 2-D fuel indicated that about 50 percent of the total composite HC emissions fell into this carbon range. Of this total, about 35 percent were composed of aldehydes, with another 40 percent being olefins which were essentially combustion products like ethylene and propylene. The remaining 25 percent were broken down evenly between paraffins and aromatics, with a small amount of other unidentified  $C_9$  and higher hydrocarbons. These probably represent the broken apart pieces of larger fuel molecules, and the small portion of unburned fuel components that are in the  $C_{10}$  and higher carbon number range.

When the catalyst was installed with 2-D fuel, the mass of total HC decreased by about 15 percent. However, the mass of speciated hydrocarbons in the  $C_1$  -  $C_{12}$  range actually increased. Figures 12 and 13 show a comparison of the seven test fuels both with and without catalyst, in terms of the total speciated







hydrocarbon mass in the  $C_1 - C_{12}$  range, and also in terms of the total ozone potential of those hydrocarbon emissions. The catalyst actually caused a 7 percent increase in the total speciated mass, and about a 15 percent increase in ozone potential, indicating the formation of more reactive species. The composition of the speciated mass shifted toward less paraffin and aromatics but more aldehydes. This indicates that this catalyst was optimized to deal with heavier unburned diesel fuel components and unburned lube oil which tend to form particulates. When dealing with the lighter combustion products and fuel components, this catalyst was only able to partially oxidize them, thus leaving behind some more reactive species than were in the engine-out exhaust. It may also indicate that some aldehydes may have formed in the catalyst due to the partial oxidation of heavier hydrocarbons. This can be seen in the higher masses of formaldehyde and acetaldehyde for 2-D fuel with the catalyst, as compared to 2-D fuel without the catalyst.

REE and RME, the neat biodiesel fuels, had a significant or noticeable effect on the speciated HC emissions, both in terms of quantity and composition. The sum of  $C_1 - C_{12}$  components accounted for nearly all of the total HC mass, indicating that very few gaseous HC species above  $C_{12}$  were present in the exhaust with REE and RME. There were also a significantly smaller number of species present, as can be seen from the graphs in Appendix C. Aldehydes and light olefins accounted for nearly 90 percent of the mass present, with the paraffins and aromatics making up only a small portion of the total mass. The overall reduction in speciated HC mass was about 40 percent for both neat biodiesel fuels, which was accompanied by a similar reduction in ozone potential. As had been the case for 2-D fuel, the catalyst was not effective in dealing with the  $C_1 - C_{12}$  hydrocarbons. With REE the catalyst tended to increase both the mass and reactivity of the  $C_1 - C_{12}$  hydrocarbons, while with RME no change was apparent.

The 50 percent blends, REE50 and RME50, were similar to the neat biodiesel fuels, in terms of  $C_1 - C_{12}$  hydrocarbons. This was true in terms of both mass and composition of the species present. The speciated mass for both REE50 and RME50 was about 40 percent lower than for 2-D fuel, as was the ozone potential. With REE50 and RME50, the  $C_1 - C_{12}$  hydrocarbons made up about 60 percent of the total HC emissions, which indicates the presence of heavier unburned fuel components, most likely due to the diesel fuel present in the blends. A few more aromatics and paraffins were present with REE50 and RME50 than for REE and RME, which also reflect the presence of the diesel fuel in the blends. However, these components were present only in very small amounts and had little effect on either total mass or reactivity. The catalyst did not appear to have any significant effect on either the mass or reactivity of the  $C_1 - C_{12}$  hydrocarbons for the 50 percent blends.

The 20 percent blends, REE20 and RME20, did not give expected emission results as established from the other biodiesel fuels. In the case of REE20,

the mass of  $C_1 - C_{12}$  hydrocarbons actually increased 13 percent compared to 2-D fuel, and was also more reactive with a 30 percent increase in ozone potential. This increase was primarily the result of a large increase in formaldehyde emissions, about twice the level measured for 2-D fuel, as well as a significant increase in several heavier aldehydes. RME20, on the other hand, appeared to have the lowest mass of  $C_1 - C_{12}$  hydrocarbons of all of the fuels, as well as the lowest ozone potential. The composition of the  $C_1 - C_{12}$  hydrocarbons with RME20 was similar to that determined for RME50 (50 percent RME). However, the mass of the species present was lower, except in the case of the aldehydes which were essentially the same for both RME50 and RME20. The total speciated mass for RME20 was about 55 percent lower, and the ozone potential was about 60 percent lower than that determined for 2-D fuel. This inconsistency in the results for REE20 and RME20 indicated the possibility of measurement error, but no error could be found in a review of the results. The reason for the unusual behavior of REE20 as compared to RME20 is not known at this time.

With the catalyst installed, REE20 and RME20 behaved in a similar manner. As would be expected, the results fell in between the tests with 2-D fuel (diesel fuel) and REE50 and RME50 (50 percent blends). This was true in terms of both speciated mass and ozone potential. The composition of  $C_1 - C_{12}$  hydrocarbons was very similar to that observed for 2-D fuel with a catalyst. Considering the fact that this catalyst does not appear effective in reducing lighter HC emissions, this result would seem to indicate that the engine out emissions were also at expected levels, which is not consistent with what the previous measurements had indicated. These results imply that the data for REE20 without catalyst may have been outliers.

## **2. $C_{13} - C_{22}$ Speciation**

The heavier hydrocarbons in the  $C_{13} - C_{22}$  range were not examined in the same manner as most of the other emissions data because the data from the GC/MS were *qualitative* rather than quantitative. However, differences between the fuels were evident on this basis, especially in the case of the neat biodiesel fuels, REE and RME.

In addition to the analysis of exhaust emissions from the various fuels, neat samples of REE and RME were diluted in laboratory reagent grade n-hexane, and subjected to GC/MS analysis. The composition of these fuels is detailed in Table 5 below.

**TABLE 5. MAJOR CONSTITUENTS OF RME AND REE FUELS**

<b>RAPESEED METHYL ESTER</b>		<b>RAPESEED ETHYL ESTER</b>	
<b>COMPOUND</b>	<b>AREA PERCENT†</b>	<b>COMPOUND</b>	<b>AREA PERCENT†</b>
7,10,13-hexadecatrienoic acid, methyl ester	0.14	dodecanoic acid ethyl ester	0.03
9-hexadecenoic acid, methyl ester	0.19	tetradecanoic acid, ethyl ester	0.04
hexadecanoic acid, methyl ester	5.96	9-hexadecenoic acid, ethyl ester	0.16
heptadecanoic acid, methyl ester	0.03	hexadecanoic acid, ethyl ester	4.98
9,12-octadecadienoic acid, methyl ester	16.87	9-octadecenoic acid, methyl ester, (Z)	0.05
9-octadecenoic acid, methyl ester	22.44	9-octadecenoic acid, ethyl ester, (Z)	30.70
octadecanoic acid, methyl ester	2.54	octadecanoic acid, ethyl ester	2.10
11-eicosenoic acid, methyl ester	16.39	1,4-cyclooctadiene	0.07
eicosanoic acid, methyl ester	1.33	11,14 Eicosadienoic acid, methyl ester	14.76
13-docosenoic acid, methyl ester	32.11	eicosanoic acid, ethyl ester	1.47
docosanoic acid, methyl ester	0.84	13-docosenoic acid, methyl ester, (Z)	39.23
15-tetracosenoic acid, methyl ester	0.54	octadecanoic acid, ethyl ester	1.39
tetracosanoic acid, methyl ester	0.12	tetracoanoic acid, ethyl ester	0.23
sum	99.5	sum	95.21
†The value area percent represents the percent for that particular compound of the total area for all compounds detected in that sample. It cannot be used for any purpose other than for discussion of the relative amount in that sample. Only those compounds for which identification with a high level of certainty are listed.			

Qualitative results of the MS analysis of the exhaust from the various fuels are given in Table 6. The results are given only as an "X" for a given compound and test run, indicating that a given compound was both detected and identified with a high degree of certainty for that test run. These results are also depicted in Figures 14 through 20, summarized in terms of the relative percent of MS response in a given sample for several general classes of compounds which were detected. REE and RME showed the least  $C_{13}$  -  $C_{22}$  hydrocarbons. Of those compounds present, long-chain normal (unbranched) alkanes made up the majority.

It would appear that many of the long-chain alkane- and alkene-based acid esters found in the fuels were fragmented at the oxygen bonds, resulting in simple alkanes and alkenes. The fuels contained several dienes but these did not appear in the exhaust. The carbon chain length in the fuels was primarily in the  $C_{20}$  to  $C_{22}$  range; however, the exhaust was primarily composed of  $C_{16}$  through  $C_{18}$  compounds. In the REE series, residual acid esters were detected in the  $C_{16}$  through  $C_{18}$  range. The catalyst-equipped runs for REE and RME were free of hydrocarbons in the  $C_{12+}$  range, indicating that the catalyst was well optimized for these compound sizes and types.

The composition of the exhaust from the remaining fuels, 2-D and all of the blends, contained many similarities, as would be expected. The exhaust from 2-D fuel appeared much like the fuel itself: many straight-chain alkanes, distributed mainly among  $C_{10}$  through  $C_{19}$  with a peak around  $C_{14}$ . Exhaust from REE50, RME50, REE20, and RME20 followed this trend also. A number of aromatic (ring-containing) compounds and substituted alkanes were also found in the exhaust from this group. It should be noted that the exhaust from the blended fuels, REE50, RME50, REE20, and RME20, did not contain any compounds that were not also found in exhaust from the neat fuels, 2-D, REE, and RME. This means that there was no apparent production of unusual and/or toxic compounds through a synergism between diesel fuel and the esters, but rather that the heavier hydrocarbons remained composed primarily of unburned fuel components.

Another important finding for the diesel-containing fuels was the large number of compounds found in the catalyst-equipped runs. While the 100 percent rapeseed esters had no compounds in the  $C_{12+}$  range, the presence of the diesel fuel component seems to have inhibited the action of the catalyst. Again, it is not possible to state whether there was any *reduction* due to the catalyst, because this work was not quantitative. However, essentially all the compounds found in the uncatalyzed runs were also found in those with the catalyst installed. As has been noted before, this catalyst was optimized to deal specifically with particle-associated hydrocarbons, and did not appear very effective in dealing with gaseous hydrocarbon emissions.





















### C. PAH Analysis

Data from PAH analysis of both gas-phase and particulate-phase samples is given in Table 7. The data for each compound measured are given as a cold-hot composite emission level in micrograms per horsepower-hour. In general, good separation was observed between gas-phase and particulate-phase compounds, with very little overlap between the PUFs and the filters. Gas -phase PAH compounds were present in much higher concentrations than the particulate-phase compounds, generally one to two orders of magnitude in most cases. Figures 21 through 26 depict PAH emissions for fuels REE, RME, REE50, RME50, REE20, and RME20 in comparison to 2-D fuel, both with and without catalyst. Because of the small relative mass of heavier compounds, all of the PAHs heavier than pyrene have been grouped and are summed under the classification “Other” on the graphs.

The 2-D fuel had a wide distribution of PAH compounds of the 18 compounds scanned for--only acenaphthene, 1-nitropyrene, and dibenzo(a,h)anthracene, were not detected. As with all of the samples, the mass of gas phase compounds was generally several orders of magnitude greater than the mass of particulate phase compounds. The catalyst was effective in reducing nearly all of the PAH compounds, generally achieving a 50 percent or better conversion efficiency.

Both neat biodiesel fuels resulted in substantial decreases in total PAH mass, 40 and 50 percent for REE and RME. A closer examination of this change reveals that this reduction occurred entirely within the gas-phase PAH compounds, except for naphthalene, which appeared unaffected by anything except the catalyst. The neat biodiesel fuels affected compounds in varying ways, with some compound levels decreasing, and others increasing. It should be noted, however that the total mass of each of these compounds was in the range of 1 microgram per horsepower-hour. The catalyst demonstrated its ability to remove PAH compounds from the exhaust, and in fact it achieved better conversion efficiency with the biodiesel fuels than with 2-D fuel. The catalyst also controlled the levels of those particulate-phase PAH compounds that had increased with the neat biodiesel fuels to levels below those observed using the 2-D fuel.

The 50 percent blends fell part way between the 2-D fuel and the neat biodiesel fuels in terms of transient cycle PAH levels. As with the neat biodiesel fuels, the reductions in mass were essentially in the gas-phase compounds except for naphthalene. RME50 achieved slightly lower levels of PAH than REE50. The particulate-phase compounds showed either no significant change, or increased to about the same levels as noted for the neat biodiesel fuels. Total mass of PAH

















emissions with the 50 percent blends was similar to levels using 2-D fuel with a catalyst. Catalyst conversion efficiency with the 50 percent blends was higher than with 2-D fuel, but somewhat lower than the levels observed for the neat biodiesel fuels.

The 20 percent blends did not result in total PAH levels significantly different from 2-D fuel; and in the case of REE20, there was actually a slight increase, due mainly to naphthalene. This correlates with the increase in speciated HC mass observed for REE20 without the catalyst. Both of the 20 percent blends had higher levels of naphthalene, but lower levels of many of the heavier gas-phase compounds. Levels observed for the particulate-phase compounds with the 20 percent blends were the same as those measured for 2-D fuel. The major difference between 2-D fuel and the 20 percent blends was that the catalyst achieved a better conversion efficiency with the 20 percent blends, as was the case for the other biodiesel test fuels.

PAH data were forwarded to Walter Switzer in the SwRI Biomedical Science group for a preliminary assessment. The assessment dealt only with the neat fuels, and the full text of that assessment is given in Appendix D. In summary, the assessment indicated that there appeared to be differences in the concentration profiles of PAHs produced by the different fuel types. This data set indicated that diesel fuel produces the lowest levels of the most potent (identified) compound, benzo(a)pyrene. However, it should be noted that none of the test fuels produced benzo(a)pyrene levels anywhere near the 10 ppb recommended exposure limit set by NIOSH. The same data set indicated that the biofuels produced lower levels of almost all the other compounds found. These assessments were based on an examination of the data, not a statistical analysis. However, the trends observed probably would benefit by at least a nonparametric analysis and further examination of the data.

## **D. Lubricity Testing**

Test results obtained from both the SLBOCLE and HFRR apparatuses are provided in Table 8. The SLBOCLE shows that all of the fuels tested had excellent lubricity. Nonetheless, the lubricity of both Biodiesel fuels was significantly better than that of the conventional diesel fuel. The REE fuel may have shown marginally better lubricity characteristics than the RME fuel. The HFRR apparatus showed directionally similar results to the BOCLE. However, the HFRR apparatus indicated that the conventional diesel fuel has only marginal to poor lubricity.

Both the SLBOCLE and the HFRR confirm that blending biodiesel with conventional diesel fuel results in a significant improvement in lubricity compared to diesel fuel alone. A slight improvement in lubricity was apparent at biodiesel concentrations down to 20 percent. Significantly more improvement would be expected if the biodiesel were blended to a very low lubricity fuel, such as kerosene.

**TABLE 8. LABORATORY SCALE WEAR TEST RESULTS**

Fuel	SLBOCLE, grams			HFRR, mm
	Run 1	Run 2	Average	
2-D	4200	4300	4250	0.405
REE	>7000	>7000	>7000	0.085
RME	7000	>7000	7000	0.140
50%RME 50%REF	5500	5600	5550	0.180
20%RME 80%REF	4500	4700	4600	0.190
50%REE 50%REF	5600	5800	5700	0.165
20%REE 80%REF	4600	4800	4700	0.165

## IV. CONCLUSIONS

In evaluating all of the results of transient testing using RME and REE, both as neat fuels and in blends, several overall points are apparent in comparing the transient emissions levels associated with biodiesel fuels to emission levels associated with diesel fuel.

The presence of oxygen in biodiesel is one of the major factors that drives many of the differences observed in transient emission levels. Figure 27 shows plots of composite HC and CO levels versus oxygen content, and Figure 28 plots total particulate emissions and the soot portion of the particulate against oxygen content. As can be seen in these graphs, increasing oxygen content results in decreased HC, CO, and particulate levels. The decrease in total particulate emissions was associated with a decrease in carbon soot levels, as shown in Figure 28.

Figure 29 shows plots of both total particulate and VOF levels as a function of the percent biodiesel in the fuel by volume. Although total particulate emissions decreased, the VOF level increased as biodiesel content increased. This increase in VOF offset the reduction in the soot portion of the total particulate, thus limiting the decrease in the total particulate level observed with biodiesel fuels. Increased levels of VOF are likely because biodiesel fuel is made up of only a narrow range of esters, around the  $C_{18}$  range. Therefore, unburned biodiesel tends to condense as particulate rather than as gaseous HC emissions.

Although there are emission advantages over diesel fuel, the disadvantages of biodiesel were a small drop in the engine performance and a worsening of BSFC (fuel economy). These changes were essentially due to the lower energy content of biodiesel fuel, as reflected by its lower heating value. Blends of biodiesel with diesel fuel lessened this impact, so that the performance of the 20 percent blends was very similar to that of diesel fuel, while engine performance with the 50 percent blends fell part way between that of neat biodiesel and diesel fuel.

Tests were also conducted on all of the fuels with the catalyst. In general, the catalyst performed better (had better conversion efficiency) when the engine was fueled on biodiesel than when fueled on diesel fuel. HC, CO, and total particulate emissions, as well as PAH, along with  $C_{13}$  and heavier hydrocarbons, were all more efficiently reduced by the catalyst. The fraction of the particulate composed of VOF increased with biodiesel fuels. With the  $C_{13}$  and heavier hydrocarbons, it may be that the species present in the exhaust, when using









biodiesel fuels, were easier for the catalyst to destroy. This would help explain the higher catalytic efficiency in reducing HC emissions. The reason for higher catalyst efficiency with biodiesel on CO and PAH emissions, and to a lesser extent HC emissions, is not readily apparent. More detailed study would be needed to fully examine the relationship between catalyst and biodiesel exhaust constituents.

Hydrocarbon speciation data indicated that biodiesel also had a beneficial effect on the character of the HC emissions, and their net ozone reactivity. With biodiesel, speciation data for hydrocarbons ranging from C<sub>1</sub> to C<sub>12</sub> carbon number indicated both a reduced mass of hydrocarbons and a reduced potential for ozone formation compared to HC emissions associated with diesel fuel. This effect appeared to increase in proportion to the amount of biodiesel in the fuel. GC/MS data for hydrocarbons having thirteen or more carbons (C<sub>13</sub>+) indicated that emissions associated with neat biodiesel fuels had far fewer species in the exhaust than when diesel fuel was used. Speciation data associated with biodiesel blends indicated that such blends did not appear to form any unusual and/or toxic hydrocarbons in the C<sub>13</sub> to C<sub>22</sub> carbon range. It should be noted that when neat biodiesel fuels and the catalyst were used, no exhaust hydrocarbons in the C<sub>13</sub> and higher carbon range were detected.

PAH data indicated that biodiesel also decreased the total transient cycle PAH levels in the exhaust. The decreases occurred mainly in the gas-phase PAH compounds, which formed the overwhelming fraction of the total PAH mass. Some of the particulate-phase compounds were reduced with biodiesel, while a few were increased. The catalyst was able to control increases levels of particulate-phase compounds associated with biodiesel. On biodiesel, the catalyst also appeared to have increased conversion efficiency for unnecessary gas-phase compounds as compared to diesel fuel.

Lubricity testing indicated that both REE and RME had excellent lubricity, and ranked better than almost all commercially available diesel fuels. Blending as low as 20 percent biodiesel with conventional diesel fuels significantly improved lubricity of the fuels.

**TABLE 1. PROPERTIES OF TEST FUELS FOR MONTANA DEQ BIODIESEL PROJECT**

Fuel	2-D	REE	RME	REE50	RME50	REE20	RME20
Description	Diesel	Neat REE	Neat RME	50% REE 50% 2-D	50% RME 50% 2-D	20% REE 80% 2-D	20% RME 80% 2-D
Fuel Code	EM-2045-F	EM-2126-F	EM-2130-F	EM-2134-F	EM-2136-F	EM-2135-F	EM-2137-F
Cetane Number, D-613	43.3	60.7	58.7	50.8	51.0	48.2	48.2
Distillation, °F, D-86:							
IBP	343	643	462	370	373	341	347
0.1	433	681	569	477	475	443	442
0.5	501	705	696	615	613	525	525
0.9	591	747	725	694	698	676	662
EP	633	763	761	714	709	687	696
API Gravity, D-4052	36	30.2	29.4	33.1	32.7	34.9	34.7
Total Sulfur, wt%, D-2622	0.03	<0.001	<0.001	0.013	0.012	0.022	0.021
Flashpoint, °F, D-1319	157	406	392	187	183	157	172
Viscosity, cSt, D-445	2.63	6.07	5.51	4.05	3.80	3.13	3.02
Carbon, wt%, D-5291	86.9	78.2	77.7	81.9	82.1	84.8	84.2
Hydrogen, wt%, D-5191	13.1	12.6	12.4	12.6	12.8	13.2	13.1
Oxygen, wt%, remainder	00.0	9.2	9.9	5.5	5.1	2.0	2.7
Heat of Combustion, Btu/lb, D-240							
Gross	19572	17483	17362	18516	18459	19131	19131
Net	18351	16336	16229	17365	17288	17930	17936
Ash Content, D-482	0.001	0.001	0.003	0.005	0.005	0.002	0.003
Carbon Residue, Ramsbottom, D-524	0.1	a	0.458	a	0.107	0.077	0.056
Cloud Point, °C, D-2500	-15	-4	-6	-8	-8	-14	-18
Pour Point, °C, D-97	-21	-18	-12	-21	-21	-21	-21

<sup>a</sup> Duplicate analyses on three different samples provided inconsistent results. No value is reported.

**TABLE 6. COMPOUNDS DETECTED AND IDENTIFIED BY MASS SPECTROGRAPHY FOR  
CUMMINS B 5.9L ENGINE WITH BIODIESEL FUELS**

Compound	2-D		2-D, Cat		REE		REE, Cat		RME		RME, Cat		REE50	
	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
2-BUTOXY ETHANOL	-	-	-	-					-	-	-	-	-	X
BENZALDEHYDE	X	X	X	X	X	X	-	-	X	-	-	-	X	X
PHENOL	X	X	-	-	-	-	-	-	-	-	-	-	-	-
DECANE	X	X	X	X	-	-	-	-	-	-	-	-	X	X
LIMONENE	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BENZALDEHYDE, METHYL	-	-	X	-	-	-	-	-	-	-	-	-	-	-
ETHANONE, PHENYL	X	-	-	-	-	-	-	-	-	-	-	-	-	-
UNDECANE	X	X	X	X	-	-	-	-	-	-	-	-	X	X
HEPENOIC ACID, ETHYL ESTER	-	-	-	-	X	X	-	-	-	-	-	-	-	-
BENZOIC ACID	X	X	-	-	X	-	-	-	-	-	-	-	X	X
NAPHTHALENE	X	X	X	X	X	-	-	-	X	X	-	-	X	X
DODECANE	X	X	X	X	-	-	-	-	-	-	-	-	X	X
DODECANE, METHYL	X	-	X	-	-	-	-	-	-	-	-	-	-	-
OCTANE, TRIMETHYL	-	-	-	-	-	-	-	-	-	-	-	-	-	-
UNDECANE, DIMEHTYL	X	X	X	X	-	-	-	-	-	-	-	-	-	-
1,3-ISOBENZOFURANDIONE	X	X	X	-	-	-	-	-	-	-	-	-	-	X
NAPHTHALENE, TETRAHYDRO-METHYL	X	X	-	-	-	-	-	-	-	-	-	-	-	-
UNDECENOIC ACID, METHYL ESTER	-	-	-	-	-	-	-	-	X	-	-	-	-	-
TRIDECANE	X	X	X	X	-	-	-	-	-	-	-	-	X	X
NAPHTHALENE, METHYL	X	X	X	-	-	-	-	-	-	-	-	-	-	-
NAPHTHALENE, TETRAHYDRO-DIMETHYL	X	X	-	-	-	-	-	-	-	-	-	-	-	-
BENZENE, BUTENYL DIMETHYL	-	X	-	-	-	-	-	-	-	-	-	-	-	-
TETRADECENE	-	-	-	-	-	-	-	-	X	-	-	-	-	-
TETRADECANE	X	X	X	X	-	-	-	-	-	-	-	-	X	X
NAPHTHALENE, DIMETHYL	X	X	-	-	-	-	-	-	-	-	-	-	X	X
1,1-BIPHENYL, METHYL	X	X	-	-	-	-	-	-	-	-	-	-	-	-
PENTADECANE	X	X	X	X	X	X	-	-	X	X	-	-	X	X
HEXADECENE	-	-	-	-	-	-	-	-	X	-	-	-	-	-
HEXADECANE	X	X	X	X	X	-	-	-	X	-	-	-	X	X
PENTADECANE, TETRAMETHYL	-	X	-	-	X	-	-	-	-	-	-	-	-	-
HEPTADECANE	X	X	X	X	X	-	-	-	-	-	-	-	X	X
OCTADECENE	-	-	-	-	-	-	-	-	X	X	-	-	-	-
OCTADECANE	-	X	-	X	X	X	-	-	X	X	-	-	X	X
NONDECANE	-	-	-	-	X	X	-	-	-	-	-	-	-	-
HEXADECANOIC, ACID, ETHYL ESTER	-	-	-	-	-	X	-	-	-	-	-	-	-	-



[illegible]



**TABLE 7. COMPOSITE PAH LEVELS FOR CUMMINS B5.9L ENGINE WITH BIODIESEL FUELS**

Fuel	Catalyst	Composite Mass (µg/hp-hr)									
		Naphthalene <sup>a</sup>	Acenaphthylene <sup>a</sup>	Acenaphthene <sup>a</sup>	Fluorene <sup>a</sup>	Fluorenone <sup>a</sup>	Phenanthrene <sup>a</sup>	Anthracene <sup>a</sup>	Fluoranthene <sup>a</sup>	Pyrene <sup>b</sup>	Benzo(a)anthracene <sup>c</sup>
2-D	No	354	83	ND	109	76	226	13	122	30	1.0
	Yes	355	30	ND	53	100	162	4	61	11	0.4
REE	No	312	52	ND	25	22	71	5	126	19	0.8
	Yes	173	9	ND	11	14	36	2	62	7	0.3
RME	No	248	37	ND	13	12	38	3	100	15	0.7
	Yes	215	11	ND	13	16	38	2	82	10	0.2
REE50	No	371	59	ND	45	36	103	7	134	23	1.3
	Yes	288	16	ND	15	22	41	1	71	9	0.4
RME50	No	357	56	ND	64	27	107	7	75	16	0.8
	Yes	214	12	ND	19	16	45	2	50	5	0.3
REE20	No	521	84	ND	98	64	170	10	129	21	1.1
	Yes	280	19	ND	28	40	74	2	62	6	0.3
RME20	No	471	71	ND	87	58	160	9	119	19	1.1
	Yes	337	19	ND	29	41	78	3	63	7	0.4
Fuel	Catalyst	Composite Mass (µg/hp-hr)									
		Chrysene <sup>c</sup>	1-Nitropyrene <sup>c</sup>	Benzo(b)fluoranthene <sup>c</sup>	Benzo(k)fluoranthene <sup>c</sup>	Benzo(e)pyrene <sup>c</sup>	Benzo(a)pyrene <sup>c</sup>	Indeno(1,2,3-cd)pyrene <sup>c</sup>	Dibenzo(a,h)anthracene <sup>c</sup>	Benzo(g,h,i)perylene <sup>c</sup>	Total PAH <sup>c</sup>
2-D	No	1.6	ND	0.8	0.6	0.5	0.3	0.4	ND	0.1	1017
	Yes	0.8	ND	0.2	0.1	ND	ND	0.2	ND	0.2	778
REE	No	1.2	ND	1.1	1.0	0.9	0.8	ND	ND	0.8	639
	Yes	0.4	ND	0.5	0.4	0.4	0.5	ND	ND	0.6	317
RME	No	1.0	ND	0.8	0.8	0.7	0.6	0.3	ND	0.6	472
	Yes	0.4	ND	0.3	0.4	0.3	0.4	0.2	ND	0.3	389
REE50	No	1.7	ND	1.2	1.2	1.1	0.9	0.4	ND	0.6	789
	Yes	0.6	ND	0.6	0.5	0.5	0.4	0.3	ND	0.5	467
RME50	No	1.1	ND	0.7	0.7	0.7	0.6	0.4	0.1	0.8	715
	Yes	0.4	ND	0.3	0.3	0.3	0.3	0.3	ND	0.4	364
REE20	No	2.1	ND	0.9	0.9	0.8	0.8	0.4	0.1	0.6	1104
	Yes	0.6	ND	0.5	0.5	0.5	0.1	0.3	ND	0.8	516
RME20	No	1.8	ND	0.8	0.7	0.7	0.7	0.4	ND	0.6	1003
	Yes	0.9	ND	0.5	0.5	0.5	1.2	0.4	ND	0.6	581

<sup>a</sup> Compounds were found in the gas-phase (PUF) samples, detection limit = 2.5 µg/hp-hr.

<sup>b</sup> Pyrene was detected in both gas-phase (PUF) samples and particulate filter samples.

<sup>c</sup> Compounds were found in the particulate-phase (filter) samples, detection limit = 0.02 µg/hp-hr.

## **APPENDIX A**

### **INDIVIDUAL TRANSIENT TEST RESULTS**

## **APPENDIX B**

### **DETAILED C<sub>1</sub> - C<sub>12</sub> SPECIATION RESULTS**

## **APPENDIX C**

### **C<sub>1</sub> - C<sub>12</sub> SPECIATION GRAPHS**

## **APPENDIX D**

### **PAH SUMMARY ASSESSMENT**

# PAH Summary Assessment

## Introduction

Data for polycyclic aromatic hydrocarbons (PAH) from diesel fuel combustion were reviewed to determine if important differences could be attributed to fuel type. Acenaphthene, 1-nitropyrene and dibenzo(a,h)anthracene were reported as 0.000, so these compounds were not included in the assessment. All the fuel combinations produced some levels of the remaining PAHs. The difference is in the amounts.

## Background

Benzo(a)pyrene has been classified as a probable human carcinogen. However, U.S. EPA has not established a Reference Dose (RfD) or a Reference Concentration (RfC) for PAH or benzo(a)pyrene. Due to the findings in studies done with benzo(a)pyrene, this compound has the lowest ranking in exposure concentration. Benzo(a)pyrene has a NIOSH (recommended exposure limit) REL of about 10 ppb or 0.1 mg/m<sup>3</sup>. This is an 8- or 10-hour time-weighted-average exposure and/or ceiling.

There is other evidence that suggests the remaining PAH compounds also present some degree of health risk. Several of the other PAHs, including benz(a)anthracene, benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, have caused tumors in laboratory animals by the oral, dermal or inhalation routes.

## Assessment

Compounds for which levels were reported as zero were dropped from the assessment. These were acenaphthene, 1-nitropyrene and dibenzo(a,h)anthracene. The remaining compounds were grouped into three categories:

1. Probable human carcinogen, benzo(a)pyrene
2. Suspect compounds: benz(a)anthracene, benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene
3. Remaining compounds: naphthalene, acenaphthylene, fluorene, fluorenone, phenanthrene, anthracene, fluoranthene, pyrene, benzo(e)pyrene and benzo(g,h,i)perylene

The assessment consisted of comparing the extremes of 3 fuel types. The category selected was 100 percent diesel versus 100 percent biofuels with no

catalysts (A-C1, B-C1, C-C1).

For the first assessment, this approach did not seem suitable for the examination of three data points, and this first comparison did not show any differences, with diesel fuel in the middle. The remaining relatable combinations of 100 percent biofuel versus 100 percent diesel fuel were examined (Table D-1) (fuel types A, B, C: -C1, C-C1, - H1, and C-H1). These data indicated that the level of benzo(a)pyrene from both the biofuels exceeded that measured from the diesel fuel.

**APPENDIX TABLE D-1. ASSESSMENT 1**

	Fuel	Catalyst	Benzo(a)pyrene, ppb
A-C1	2-D	No	3.12
A-H1		No	0.14
AC-C1		Yes	1.13
AC-H1		Yes	ND
B-C1	REE	No	3.21
B-H1		No	0.95
BC-C1		Yes	1.82
BC-H1		Yes	0.56
C-C1	RME	No	2.85
C-H1		No	0.64
CC-C1		Yes	1.77
CC-H1		Yes	0.44
ND = Not Detected			

The second assessment (Table D-2) for comparison of A-C1, B-C1, and C-C1 displayed the opposite trend. The biofuels produced lower levels of these compounds than the equivalent diesel fuel combination for all the PAH in this category.

The third assessment (Table D-3) supports the findings of the second assessment for the A-C1, B-C1, and C-C1 comparison. The biofuels produced fewer of these PAHs than the diesel fuel except for benzo(e)pyrene and benzo(g,h,i)perylene, which were among the highest molecular weight compounds in this group.

**APPENDIX TABLE D-2. ASSESSMENT 2**



Compound, ppm	2-D	REE	RME
Chrysene	0.00626	0.00365	0.00348
Benzo(a)anthracene	0.00493	0.00276	0.00280
Benzo(b)fluoranthene	0.00502	0.00385	0.00294
Indeno(1,2,3-cd)pyrene	0.00231	0.00119	0.00174
Benzo(k)fluoranthene	0.00439	0.00367	0.00330

**APPENDIX TABLE D-3. ASSESSMENT 3**

Compound, ppm	2-D	REE	RME
Naphthalene	1.5463	0.8637	1.0088
Acenaphthylene	0.4364	0.1971	0.1702
Fluorene	0.3801	0.0621	0.0364
Fluorenone	0.2456	0.0490	0.0261
Phenanthrene	0.7367	0.1728	0.1014
Anthracene	0.0680	0.0199	0.0137
Fluoranthene	0.6652	0.4140	0.3679
Pyrene	0.0938	0.0501	0.0492
Chrysene	0.0063	0.0036	0.0035
Benzo(e)pyrene	0.0029	0.0032	0.0027
Benzo(g,h,i)perylene	0.0023	0.0030	0.0025

## Summary

There appears to be differences in the concentration profiles of PAHs produced by the fuel types. This data set indicates that diesel fuel produces the lowest levels of the most potent (identified) compound, benzo(a)pyrene. However, the same data set indicates the biofuels produce lower levels of almost everything else. These assessments were based on an examination of the data, not a statistical analysis. However, the trends observed would probably benefit by at least a nonparametric analysis and further examination of the data.